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DESORPTION RESISTANCE OF POLYCYCLIC AROMATIC HYDROCARBONS AND DURATION OF EXPOSURE

Yunzhou Chai,† Alexander Kochetkov,‡ and Danny D. Reible*§

†Toxicology and Environmental Research & Consulting, The Dow Chemical Company, Midland, Michigan 48674, USA
‡Institute for Experimental Meteorology TYPHOON, Obninsk, Russia
§Department of Civil, Architectural, and Environmental Engineering, University of Texas at Austin, Austin, Texas 78713, USA

Abstract—The desorption-resistant fraction of laboratory-spiked phenanthrene in two Louisiana (USA) sediments was not observed to be significantly different, but the two sediments exhibited different condensed-phase organic carbon contents, as defined operationally by the organic carbon remaining after combustion of the sediment at 375°C. Only 3% of the original saturated phenanthrene in the sediments was not readily removed by exposure to a nonpolar polymeric resin and sorbent XAD-2. Allowing the laboratory-spiked contaminants to age for periods of up to three years yielded little difference in the desorption-resistant characteristics of the sediments. Field-contaminated sediments from Utica Harbor (Utica, NY, USA) and Rouge River (Detroit, MI, USA) that had a lengthy (decades to a century) period of contamination, however, exhibited significantly different desorption-resistant contaminant fractions, consistent with the fractions of condensed-phase organic carbon in the sediments. Measurements of the fraction that could be rapidly desorbed using the XAD-2 sorbent also accounted for essentially all desorption to pore water and, thus, provided a good prediction of effective bulk partition coefficients. It was concluded that the condensed-phase organic carbon was a good indicator of the potential for desorption resistance in field-contaminated sediments and that the rapidly desorbing fraction provided a quantitative indicator of its significance.

Keywords—Hydrophobic organic contaminants   Sediments   Availability   Desorption   Condensed-phase organic carbon

INTRODUCTION

Recent research has revealed that the availability of sediment- or soil-associated hydrophobic organic contaminants (HOCs), but not the total concentration of sediment- or soil-associated contaminants, is critical to define the exposure, uptake, or risk of contaminants to receptor organisms in the environment. To a great degree, physicochemical availability of sediment- or soil-bound contaminants controls their bioavailability, because the partitioning of contaminants between the solid and water phases is a key indicator of the potential for exposure and risk [1–4].

In evaluating contaminant fate, risk, and endpoints for remediation, the total solid-phase concentration often has been used and linear partitioning assumed [5]:

$$C_S = K_P C_W = K_{OC} f_{OC} C_W \qquad (1)$$

where C_S is the contaminant concentration associated with the soil or sediment phase (mg/kg), C_W is the aqueous concentration (mg/L), f_{OC} is the mass fraction of organic carbon in a sediment/soil, and K_P is the equilibrium sediment/soil–water partition coefficient (L/kg). Because most HOCs reside in soil/sediment organic matter in natural sorbents [6,7], when the f_{OC} of the sediment or soil is greater than 0.1% [8], the organic carbon–normalized sediment– or soil–water partition coefficient (K_{OC}) is more frequently used to characterize the sorption capacity of a certain HOC compound in a sediment or soil. This linear and reversible partitioning model [5] suggests that 100% of the sediment- or soil-associated HOC is available for partitioning into the mobile phase. Evidence is increasing,

however, that a fraction of the sediment- or soil-bound HOC is not easily desorbed, which results in reduced availability of the desorption-resistant fraction of HOC [2,4,9–13]. Thus, the linear and reversible partitioning model would no longer be appropriate to describe desorption of HOC from the resistant compartment. Biphasic or triphasic empirical models have been proposed to describe both the rapid release of the reversible or labile fraction (governed by Eqn. 1) followed by a slow and more limited release of the resistant fraction [14–16]. However, these empirical kinetic models have not revealed the mechanism for the desorption resistance of HOCs in sediments or soils.

The desorption-resistant fraction has been suggested to be related to the heterogeneity of organic matter in sediment or soil. The fraction of organic matter that includes diagenetically young, natural sorbents is generally amorphous and is volatile after exposure to 375°C for 24 h with plenty of air [17]. In addition to the amorphous natural organic matter, a condensed organic carbon phase, also characterized as hard carbon, aged carbon, black carbon, or glassy polymeric carbon, often is present as well, and this phase also often is associated with anthropogenic sources of carbon, such as soot or diagenetically aged, natural sorbents. This material has been postulated to be responsible for the desorption resistance of HOCs in sediments or soils [17–24]. The condensed-phase organic carbon exhibits extremely high sorption capacity, as indicated by an elevated partition coefficient [13,25], and it is highly reduced and condensed in form so that the diffusion rate of contaminants in this phase is extremely slow [20]. The condensed-phase organic carbon has been defined operationally by the nonvolatile fraction of organic carbon remaining after sediment is combusted at 375°C for 24 h with plenty of air [17],

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* To whom correspondence may be addressed
(reible@mail.utexas.edu).

and the usefulness of this operational definition is evaluated further herein.

Thus, the characteristics of desorption, specifically the readily released and desorption-resistant fraction of contaminant and the effective partition coefficient, should be related to the condensed-phase organic carbon in sediment. The present study was directed toward characterizing the relationship between the desorption-resistant phenomena and the quality of the sediment organic matter, specifically as measured by the condensed-phase organic carbon content (f_{OC}^C), as defined by the thermal oxidation method described by Gustafsson et al. [17]. Two laboratory-spiked sediments, from Bayou Manchac (BM; LA, USA) and University Lake (UL; LA, USA), were spiked with phenanthrene (PHE), a sediment-associated hydrophobic polycyclic aromatic hydrocarbon (PAH). The kinetics of desorption determined using a nonpolar polymeric sorbent XAD-2 resin were compared for these two sediments for both freshly spiked and equilibrated (equilibration extending for up to three years) samples. The desorption characteristics of several PAHs in two field-contaminated sediments with a long history of contamination, Utica Harbor (UH; Utica, NY, USA) and Rouge River (RR; Detroit, MI, USA), also were contrasted with those of the laboratory-spiked sediments.

MATERIALS AND METHODS

Sediments

Two clean sediments, BM and UL, were used in the present study for spiking of PHE as a tracer contaminant. Sediment from BM, a freshwater bayou in Baton Rouge (LA, USA), was collected in 1998, and sediment from UL, a freshwater lake in Baton Rouge, was collected in 1999. Originally, these sediments were free of contaminants; in particular, they contained less than 0.01 mg/kg of PHE. After sieving using a 2-mm sieve, BM and UL sediment were spiked with PHE (purity, 98%; Sigma-Aldrich Chemical, Milwaukee, WI, USA) as a model contaminant using procedures described previously [2]. Phenanthrene was dissolved in hexane and transferred into a 4-L glass jar, then evaporated under a stream of ultrahigh-purity nitrogen while rotating the jar until PHE uniformly deposited on the internal wall of the glass jar. Preweighed sediment with known moisture content (45–55% water/wet sediment wt) and sodium azide (3,000 mg/kg dry sediment wt) were added into the glass jar and mixed homogeneously and manually. The glass jar was then tumbled for five weeks to ensure that PHE partitioned homogeneously to the matrices of sediment. The amount of sodium azide added was sufficient to inhibit microbial activities in that the PHE concentration in sediment remained stable during tumbling [2]. Spiked sediments were stored in darkness at 4°C for aging. Aged BM sediment was stored for three years and UL sediment for two years.

Two field-contaminated sediments, UH and RR, also were used in the present study. Sediment that was contaminated over many decades during the operation of a coal gasification plant was collected from UH. Sediment that was contaminated throughout the 20th century by both municipal and industrial discharges was collected from RR. Both sediments were passed through a 2-mm sieve to remove debris before use and were stored at room temperature in tightly sealed barrels with overlying water to avoid air drying. Sodium azide (3,000 mg/kg dry sediment wt) was added to inhibit microbial activities in the desorption experiment.

Measurement of organic carbon content

The total organic carbon content of sediment was analyzed in triplicate on a PerkinElmer 2400 Series II CHN elemental analyzer (PerkinElmer, Norwalk, CT, USA). Preliminary tests showed that acidifying samples did not significantly change measured organic carbon contents, indicating that inorganic carbon contents in the sediments used for the present study were negligible. Thus, sediment samples were not acidified before analysis.

The condensed-phase or nonvolatile organic carbon content of sediment was measured using the thermal oxidation method as described previously by Gustafsson et al. [17]. The organic carbon content was measured in triplicate after the sediment was combusted at 375°C for 24 h with plenty of air. The amorphous organic carbon content (f_{OC}^A) and the condensed-phase organic carbon content (f_{OC}^C) of the sediment were calculated from the measured total organic carbon content of the sediment before (f_{OC}) and after (f_{OC}^{375}) combustion at 375°C, considering the weight loss of the sediment during the combustion process. The fraction of oxidizable organic carbon at 375°C was considered to be the volatile or amorphous organic carbon fraction. This could possibly include the soft carbon [18], natural organic matter [17], or rubbery-phase organic matter [22], which exhibits no desorption resistance and partition coefficient consistent with the literature value. Condensed-phase organic matter was used to denote the organic matter that was not oxidizable or not volatile at 375°C. This could include hard carbon [18], black carbon or soot carbon [17], coal-derived particles [20], or glassy-phase organic matter [22]. They are in a reduced and condensed form, and may exhibit much stronger association of HOCs in sediment. Although this procedure for separating amorphous and condensed-phase organic carbon is commonly used [26–28], it is simply an operational definition, the usefulness of which is evaluated further in the present study.

Chemical analysis

For sediment samples, ultrasonic extraction as suggested by U.S. Environmental Protection Agency (Method 3550B, SW-846 [29]) was used to extract PAHs from sediment matrix. The extraction efficiencies for PHE were 96.6% ± 5.0% and 93.5% ± 1.1% from freshly spiked and aged laboratory sediments, respectively (mean ± standard deviation throughout). An Agilent 1100 Series high-performance liquid chromatograph (HPLC; Agilent, Palo Alto, CA, USA) equipped with an ultraviolet diode-array detector and fluorescence detector was used to determine the concentration of contaminant in the extract following the method suggested by U.S. Environmental Protection Agency (Method 8310, SW-846 [30]). The concentration of contaminant in the aqueous phase was measured directly by the HPLC after centrifugation (2,000 *g*, 20 min).

Desorption kinetics

Desorption kinetics were determined by mixing sediments with Amberlite XAD-2 (Supelco, Bellefonte, PA, USA), a nonpolar polymer resin sorbent. Amberlite XAD-2 was used as an essentially infinite sink to maintain the pore water adjacent to the desorbing solid at a concentration of effectively zero. A certain amount of sediment, usually 100 to 200 g of wet sediment (moisture content of 40–50% wet wt), was placed in a glass jar and mixed homogeneously with 10% (dry mass ratio) XAD-2. Preliminary studies showed that this level of

XAD-2 loading was sufficient to capture all desorbed HOCs within the duration of the experiment. The glass jar containing sediment amended with XAD-2 was sealed using an aluminum foil–lined screw cap and placed in an incubator at 25°C. At designated times (from 20 h to 60 d), sediment and XAD-2 were separated in the following manner: 100 ml of cesium chloride solution with a density of 1.1 g/ml were added into 20 g of the sediment amended with XAD-2 resin and mixed thoroughly using a magnetic stirring bar. The mixture was then allowed to settle for 10 to 15 min, until the XAD-2 floating on the surface could be clearly separated from the sediment suspension. The sediment was separated from the cesium chloride solution by centrifugation (2,000 *g,* 20 min) and washed with tap water three times to remove any residual salt. Sediment was then collected to measure chemical concentrations and moisture content in triplicates.

Measurement of apparent partition coefficient

The apparent sediment–water partition coefficients for contaminants were measured in triplicates according to the standard procedures of the American Society for Testing and Materials [31]. Two grams of wet sediment (moisture content of ~40% wet wt) with a known initial contaminant concentration were placed into a 50-ml, amber-glass bottle with a Teflon®-lined screw cap. The bottle was then filled with electrolyte solution (0.01 M NaCl, 0.01 M CaCl$_2$·2H$_2$O, and 0.01 M NaN$_3$ in deionized water) with minimal headspace. At the end of the equilibration time of 10 d, the sediment slurry was centrifuged (2,000 *g,* 20 min). Aqueous samples were then taken from each bottle, and the contaminant concentration in the aqueous phase was analyzed by HPLC as described above. The truly dissolved aqueous-phase concentration was estimated from the total aqueous-phase concentration by correcting for partitioning to dissolved organic carbon in the samples according to the method described by Lu et al. [4]. The effective partition coefficient to the dissolved organic carbon was estimated to be 0.58 log units less than the organic carbon–based partition coefficient [32]. Although this approximation is potentially subject to error, the maximum magnitude of this correction to the sediment–water partition coefficient was only 0.17 log units (for the strongly hydrophobic benzo[*a*]pyrene [B*a*P]) because of the low dissolved organic carbon concentration (2 mg/L). The contaminant concentration in sediment at the completion of equilibration was calculated based on mass balance assuming that no loss of compounds of interest occurred during equilibration. Lu et al. [2,4] showed that closure of the mass balance by these methods for PHE and B*a*P after a 10-d equilibration using these procedures was greater than 95% [2] and 90% [4], respectively.

Data analysis

Desorption kinetics for freshly spiked and aged BM and UL sediments were fitted to the biphasic kinetics as depicted in Equation 2 [14,15]:

$$\frac{S_t}{S_0} = 1 - Fe^{-k_f t} - (1 - F)e^{-k_s t} \tag{2}$$

where *t* is time (h), S_t is the mass of contaminant removed by sorbent at time *t*, S_0 is the total initial mass of contaminant in sediment, S_t/S_0 is the fraction of contaminant released after time *t*, *F* is the fraction of contaminant released quickly, (1 − *F*) is the fraction of contaminant released slowly, and k_f and k_s are the first-order rate constants describing the fast- and

slow-releasing fractions, respectively (1/h). The fast-desorbing fraction (*F*) and the first-order rate constants for the fast-desorbing fraction (k_f) and the slow-desorbing fraction (k_s) were determined by least-square optimization. Triphasic desorption kinetic models also have been reported [33,34], but the biphasic model gave very good correlation, with r^2 values greater than 0.99 for all sediments.

Because of the relatively small fast-desorbing contaminant fraction for field-contaminated sediments (UH and RR), *F* was defined operationally by Equation 3:

$$F = \frac{C_0 - C_{Des}}{C_0} \tag{3}$$

where C_0 (mg/kg) is the initial concentration of a contaminant in sediment and C_{Des} (mg/kg) is the concentration of a contaminant in sediment after sorbent-assisted desorption for 20 h. A preliminary experiment showed that 20 h with the XAD-2 sorbent was sufficient to remove essentially all the fast-desorbable fraction and that longer exposures to XAD-2 produced little additional desorption.

Because the measured organic carbon–normalized partition coefficient in a short-term partitioning experiment is governed by the fast-desorbing fraction, this fraction should be related to the effective bulk partition coefficient. If only the labile, fast-desorbing fraction ($C_{S,fast}$) contributes to the pore-water concentration, the pore-water concentration should be

$$C_W = \frac{C_{S,fast}}{f_{OC} K_{OC,lit}} \tag{4}$$

where the $K_{OC,lit}$ is the partition coefficient reported in the literature and is calculated from the octanol–water partition coefficient (K_{OW}) [35] using Equation 5 [5]:

$$\log K_{OC,lit} = \log K_{OW} - 0.21 \tag{5}$$

Thus, the predicted apparent bulk K_{OC} is given by

$$K_{OC,bulk,pred} = \frac{C_S}{C_W f_{OC}} = \frac{C_S}{\dfrac{C_{S,fast}}{f_{OC} K_{OC,lit}} f_{OC}} = \frac{C_S}{\dfrac{C_S F}{K_{OC,lit}}} = \frac{K_{OC,lit}}{F} \tag{6}$$

and

$$\log K_{OC,bulk,pred} = \log K_{OC,lit} - \log F \tag{7}$$

RESULTS AND DISCUSSION

Desorption kinetics and condensed-phase organic carbon fraction in laboratory-spiked sediments

Organic carbon contents of the two laboratory-spiked sediments, BM and UL, are presented in Table 1. The two sediments exhibited significantly different total organic carbon contents and amorphous/condensed-phase organic carbon ratios. The BM sediment had a total organic carbon content of 1.54% ± 0.02%, 48% of which was condensed-phase organic carbon, whereas UL sediment had a total organic carbon content of 6.35% ± 0.12%, 13% of which was condensed-phase organic carbon.

Desorption kinetics determined using the nonpolar sorbent Amberlite XAD-2 for freshly spiked BM and UL sediments are shown in Figure 1. The fraction of PHE desorbed from the two sediments after 20 h of exposure to XAD-2 was essentially identical (97% desorbed). Essentially no desorption-resistant fraction was detected in either spiked sediment, presumably because of the short period of exposure during spiking (approximately five weeks). The relatively high spiked con-

Table 1. Total organic carbon and condensed-phase organic carbon contents of sediments[a]

Sediment	f_{OC} (%)	f_{OC}^{A} (%)	f_{OC}^{C} (%)	f_{OC}^{C}/f_{OC} (%)
BM	1.54 ± 0.02	0.80 ± 0.03	0.74 ± 0.02	48.05 ± 1.47
UL	6.35 ± 0.12	5.52 ± 0.12	0.83 ± 0.01	13.07 ± 0.54
UH	2.10 ± 0.02	1.28 ± 0.03	0.82 ± 0.02	39.07 ± 1.02
RR	7.90 ± 0.17	5.93 ± 0.17	1.97 ± 0.02	24.89 ± 0.59

[a] Data were obtained in triplicates. Values are presented as the mean ± standard deviation. f_{OC}: total organic carbon content of sediment; f_{OC}^{A}: amorphous organic carbon content as defined by the fraction lost at 375°C; f_{OC}^{C}: condensed-phase organic carbon contents defined by fraction retained at 375°C. BM = Bayou Manchee, LA, USA; UL = University Lake, LA, USA; UH = Utica Harbor, Utica, NY, USA; RR = Rouge River, Detroit, MI, USA.

centration, however, also may have limited the observable influence of the desorption-resistant fraction of contaminants. Cornelissen et al. [36] emphasize that the relative importance of the desorption-resistant fraction is largest at low concentrations.

Desorption kinetics also were determined for aged BM and UL sediments. Spiked BM sediment was aged for three years and spiked UL sediment for two years. Desorption kinetics for freshly spiked and aged BM and UL sediments were fitted to the biphasic kinetics depicted in Equation 2. As shown in Table 2, fast-desorbing fractions for the freshly spiked BM and UL sediments were 0.964 and 0.971, respectively. This indicated that approximately 3% of PHE in BM and UL sediments was desorption resistant, as determined by XAD-2 desorption, showing no significant difference for the two sediments. The rate constants for the fast-desorbing fraction were 0.108 and 0.114/h for BM and UL sediment, respectively, and the rate constants for the slow-desorbing fraction were 6.06×10^{-4} and 6.58×10^{-4}/h, respectively. Fast-desorbing fractions for the aged BM and UL sediments were both 0.915/h, again indicating no difference between the two sediments despite approximately 8% of the PHE being associated with a desorption-resistant fraction.

The absence of a difference between the sediments was unexpected, because these two sediments showed a significant

variation in condensed-phase organic carbon contents (f_{OC}^{C}/f_{OC}). This might result from the very slow diffusion rate in the condensed-phase organic matter particles, which is responsible for the desorption resistance. Even an aging period of three years was apparently insufficient to show a significant aging effect. Ghosh et al. [20] used cryomicrotome technique and microprobe two-step laser-desorption/laser-ionization mass spectrometry to investigate the cross-sectional distribution of PAHs in coal-derived particles, and their results suggested that most PAHs are concentrated in the near-external-surface regions of coal-derived particles. The presumption of slow diffusion of the contaminants in coal-derived particles was supported by their modeling results, which showed 40% PAH remaining in sediment even after 100 years [20]. In this context, the time scale of exposure during spiking of five weeks— and even during the aging time of two or three years—was too short a period to cause significant migration of PHE into the condensed-phase organic matter by diffusion. Another confounding factor was that the PHE concentrations spiked in the two laboratory-contaminated sediments were near saturation concentrations. This might have masked the effect of condensed-phase organic carbon. It has been reported [36] that the contribution of the condensed-phase organic carbon (non-amorphous organic carbon) to the PHE sorption in a sediment is dominant when the corresponding aqueous concentration is less than 1 µg/L. The contribution of the condensed-phase organic carbon is reduced dramatically as the corresponding aqueous-phase concentration approaches the aqueous solubility of PHE [37]. Because of the much greater sorption capacity typically reported for the condensed-phase organic carbon, however, one would expect that even high concentrations ultimately would exhibit the effects of desorption resistance from this phase. A three-year aging period was apparently insufficient at these high sorbed concentrations, however, and lower concentrations might be required to see such effects. For the
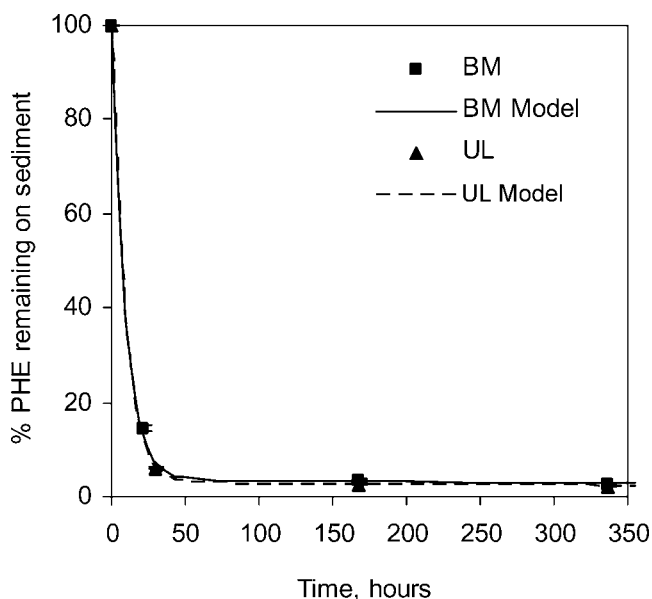

Fig. 1. Biphasic desorption kinetics of phenanthrene (PHE) from freshly spiked Bayou Manchac (BM; LA, USA) and University Lake (UL; LA, USA) sediment. Data points were experimental data and lines were calculated from biphasic first-order model as described in Equation 2.

Table 2. Fitting parameters for desorption kinetics of phenanthrene from freshly spiked and aged Bayou Manchee (BM; LA, USA) and University Lake (UL; LA, USA) sediments using simple empirical biphasic model[a]

Sediment	F	k_f (h^{-1})	k_s (h^{-1})	r^2
Fresh BM	0.964	0.108	6.06×10^{-4}	0.999
Aged BM	0.915	0.102	6.14×10^{-4}	0.998
Fresh UL	0.971	0.114	6.58×10^{-4}	0.999
Aged UL	0.915	0.074	1.55×10^{-3}	0.999

[a] These parameters were obtained by fitting experimental data to the biphasic kinetics depicted in Equation 2 utilizing Excel Solver (Microsoft, Redmond, WA, USA) to optimize the fast-desorbing fraction (F), the rate constant for the fast fraction (k_f), and the rate constant for the slow fraction (k_s).

Table 3. Fast desorbing fractions of polycyclic aromatic hydrocarbons in Utica Harbor (Utica, NY, USA) and Rouge River (Detroit, MI, USA) sediment[a]

Compound	Utica Harbor sediment			Rouge River sediment		
	C_0 (mg/kg)	C_{Des20h} (mg/kg)	F	C_0 (mg/kg)	C_{Des20h} (mg/kg)	F
Phenanthrene	6.53 ± 0.22	5.07 ± 0.12	0.22 ± 0.01	22.93 ± 0.48	12.77 ± 0.19	0.44 ± 0.01
Anthracene	5.80 ± 0.10	4.16 ± 0.14	0.28 ± 0.01	8.05 ± 0.23	4.25 ± 0.17	0.47 ± 0.02
Pyrene	23.75 ± 0.45	18.25 ± 0.34	0.23 ± 0.01	36.51 ± 1.25	24.73 ± 0.88	0.32 ± 0.02
Chrysene	24.25 ± 1.03	17.22 ± 0.75	0.29 ± 0.02	22.44 ± 1.01	13.94 ± 0.32	0.38 ± 0.02
Benzo[b]fluoranthene	8.91 ± 0.31	4.83 ± 0.19	0.46 ± 0.02	15.43 ± 0.54	9.54 ± 0.29	0.38 ± 0.02
Benzo[k]fluoranthene	4.15 ± 0.05	3.68 ± 0.06	0.11 ± 0.01	8.75 ± 0.37	5.63 ± 0.16	0.36 ± 0.02
Benzo[a]pyrene	12.67 ± 0.36	9.29 ± 0.33	0.27 ± 0.01	11.60 ± 0.28	8.81 ± 0.35	0.24 ± 0.01

[a] Data were obtained in triplicates. Values are presented as the mean ± standard deviation. C_0: initial concentration of contaminant in sediment; C_{Des20h}: concentration of contaminant in sediment after treatment with XAD-2 for 20 h; F: fast-desorbing fraction, operationally defined as $(C_0 - C_{Des20h})/C_0$.

purposes of the present work, however, the influence of desorption resistance was assessed by observations with field-contaminated sediment not subject to these limitations.

Fast-desorbing fraction and condensed-phase organic carbon fraction in field-contaminated sediments

The fraction desorbed after 20 h of exposure to XAD-2 and the effective sediment–water partition coefficient were determined for a variety of PAHs from the field-contaminated sediments. To minimize errors at the low-desorption fraction, only compounds for which effective sediment–water partition coefficients could be measured were included in the analysis. The fast-desorbing fractions of PAHs of interest ranged from 0.11 to 0.46. in UH sediment (slow-desorbing fraction of 0.89–0.54), although all except two benzofluoranthenes indicated fast-desorbing fractions of between 0.22 and 0.29. The rapid-desorbing fraction of the PAHs varied from 0.21 to 0.44 in RR sediment (slow-desorbing fraction of 0.79–0.56), although only B*a*P exhibited a fast-desorbing fraction of less than 0.32 (Table 3). The apparently anomalous behavior of these more-sorbing PAHs may have been associated with slow desorption kinetics, but all data for which a desorption fraction and a partition coefficient were measured were included in subsequent statistical analyses.

The average of the fast-desorbing fractions for all compounds in each of the UH and RR sediments was 0.265 ± 0.11 and 0.37 ± 0.08, respectively. A statistical analysis (two-sample, *t* test) was used to evaluate the hypothesis that the UH sediment showed a significantly smaller fast-desorbing fraction of PAHs. The difference was shown to be significant ($p = 0.035$), consistent with the lower proportion of amorphous-phase organic carbon (f_{OC}^C/f_{OC}) in the UH sediment (61% vs 75%), as shown in Table 1. Because it is expected that the condensed-phase organic carbon has a higher capacity for the contaminants, the fast-desorbing contaminant fraction would be expected to be smaller than rather than equal to the fraction of amorphous organic carbon, as observed. The data do, however, support the concept that desorption resistance increases with the fraction of condensed-phase organic carbon, as indicated by the fraction of organic carbon not volatilized at 375°C. The influence of this measure of condensed-phase organic carbon and desorption resistance on bioavailability is currently under study.

The direct use of the rapidly desorbed fraction to estimate the effective partition coefficient through Equation 7 also was tested for the UH and RR sediments (Fig. 2). The predicted log $K_{OC,bulk,pred}$ values were approximately identical to those

observed experimentally, as shown by the parity line in the Figure 2. The best-fit linear-regression line exhibited a slope of 0.99, close to the model value of unity, with a r^2 value of 0.89. This observation suggested that the labile, fast-desorbing fraction of the contaminants associated with the sediments controlled the short-term release and was a good predictor of the effective partition coefficient. Alternatively, the results suggest that the desorption-resistant fraction of contaminants contributed essentially nothing to the measured effective sediment–water partition coefficient.

Lu et al. [2] showed that it is appropriate to use the pore-water concentration to predict bioavailability of HOCs to sediment-dwelling organisms, regardless of whether the uptake is via sediment ingestion or sorption from pore water. It has been shown above that the fast-desorbing fraction indicated the portion of contaminants readily available for partitioning into pore water. In this context, for a specific contaminant, one would expect reduced bioavailability for sediments with smaller fast-desorbing fractions. The fast-desorbing fraction of PAHs extracted from marine sediment by Tenax TA® (Baltimore, MD, USA) has been shown to be related to the fraction susceptible to biodegradation by microorganisms [38]. The accumulation
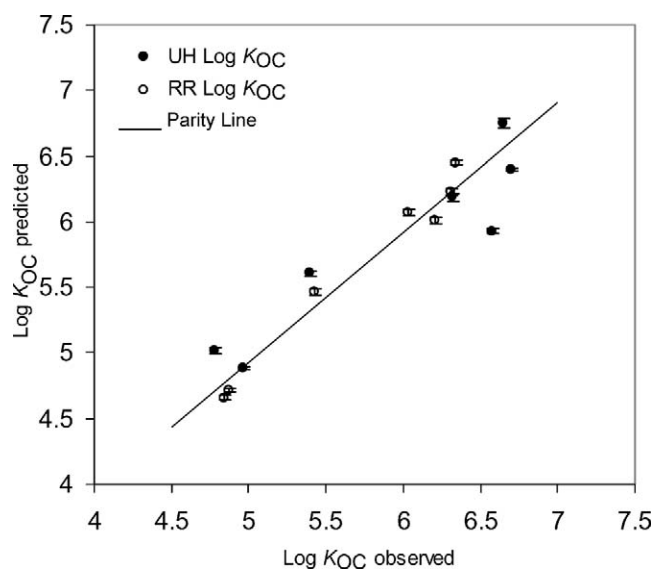

Fig. 2. Predicted and observed effective partition coefficients for Utica Harbor (UH; Utica, NY, USA; solid circles) and Rouge River (RR; Detroit, MI, USA; open circles) sediment. The solid line indicates log K_{OC} predicted = observed. Shown is the linear regression for both UH and RR sediment, slope of 0.99 ($r^2 = 0.89$).

of polychlorinated biphenyls, PAHs, and linear alkylbenzenes from sediment to a deposit-feeding bivalve has been found to correlate with the fraction desorbed to XAD resin in 48 h [39]. Lei et al. [40] reported that field-contaminated sediments with PAHs subjected to both desorption by XAD resin and biodegradation exhibit similar residual concentrations of PAHs, indicating that the fast-desorption fraction is an indication of availability.

CONCLUSIONS

The desorption resistance of laboratory-spiked contaminants in BM and UL sediments was not observed to be significantly different, but the two sediments have different condensed-phase organic carbon contents based on the carbon remaining after combustion at 375°C. Only 3% of the original PHE in BM and UL sediments exhibited desorption-resistant phenomena based on desorption kinetics after five weeks of aging. Sediment aged up to three years exhibited a slightly higher desorption-resistant fraction of contaminants for both BM and UL sediments, but again, no significant differences were noted between the sediments despite the different condensed-phase organic carbon contents. The absence of a correlation between desorption resistance and the condensed-phase organic carbon content in laboratory-spiked BM and UL sediment may have been caused by the extremely slow diffusion rate of contaminant in the condensed-phase organic carbon, but it also may have been the result of dominance of the fast-release fraction at the high-spiked concentrations.

The ability of this measure of condensed-phase organic carbon to predict desorption resistances also was tested with field-contaminated sediments (UH and RR) that had a lengthy (decades) period of exposure. The field-contaminated sediments showed significantly different desorption-resistant behavior. The UH sediment exhibited a more pronounced desorption-resistant behavior (i.e., greater fractions of contaminants desorbed slowly or not at all over the course of the experiments), consistent with its greater fraction of condensed-phase organic carbon. The effective partition coefficient for individual PAH contaminants also was shown to be consistent with a model assuming that only the fraction of contaminants associated with the amorphous organic carbon described the fast-desorbing fraction and was responsible for measured pore-water concentrations. Thus, the results indicate the partitioning fraction of contaminants in aged field sediments can be directly related to the rapid-release fraction of contaminants from such sediments and is consistent with the fraction of condensed-phase organic carbon, as measured by combustion at 375°C.

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